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(54) Title: LIQUID DETERGENTS WITH N-ALKOXY OR N-ARYLOXY POLYHYDROXY FATTY ACID AMIDE SURFACTANTS		
<p>(57) Abstract</p> <p>Liquid laundry detergent compositions comprising conventional anionic surfactants, various optional deterative adjuncts such as builders, enzymes, brighteners and the like, together with fluid carriers are prepared using N-alkoxy or N-aryloxy polyhydroxy fatty acid amide surfactants. Amide surfactants such as the palm oil fatty acids of N-(3-methoxypropyl) glucamide and N-(2-methoxyethyl) glucamide are also employed in anionic-free liquid detergents, which are characterized by their good cleaning performance and relatively low viscosities, even in concentrated form.</p> <p style="text-align: center;">BEST AVAILABLE COPY</p>		

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LIQUID DETERGENTS WITH N-ALKOXY OR N-ARYLOXY
POLYHYDROXY FATTY ACID AMIDE SURFACTANTS

FIELD OF THE INVENTION

5 The present invention relates to liquid detergents which are especially useful for laundering fabrics.

BACKGROUND OF THE INVENTION

Considerable success in the formulation of detergent compositions has recently been achieved using the N-alkyl polyhydroxy fatty acid amide surfactants. However, even these superior surfactants do suffer from some drawbacks. For example, their solubility is not as high as might be desired for optimal formulations. At high concentrations in water they can be difficult to handle and pump, so additives must be employed in manufacturing plants to control their viscosity. While quite compatible with anionic surfactants, their compatibility can be diminished substantially in the presence of water hardness cations. In addition, there is always the objective to find new surfactants which lower interfacial tensions to an even greater degree than the N-alkyl polyhydroxy fatty acid amides in order to increase cleaning performance.

It has now been determined that the N-alkoxy and N-aryloxy polyhydroxy fatty acid amide surfactants surprisingly differ from their counterpart N-alkyl polyhydroxy fatty acid amide surfactants in several important and unexpected ways which are of considerable benefit to detergent formulators. The alkoxy and aryloxy-substituted polyhydroxy fatty acid amide surfactants herein substantially reduce interfacial tensions, and thus provide for high cleaning performance in detergent compositions, even at low wash temperatures. The surfactants herein exhibit increased compatibility with other deterative ingredients, even in the presence of water hardness cations such as calcium and magnesium ions. This means that the compositions herein can be more effective even under the so-called "underbuilt" situation that occurs with many nonphosphate builders. Quite unexpectedly, the surfactants herein exhibit improved solubility in water over the corresponding N-alkyl polyhydroxy fatty acid amide surfactants, even at low temperatures (5°-30°C). The high solubility of the surfactants herein allows them to be formulated as highly concentrated liquid detergents. Moreover, the surfactants herein can be easily prepared as low viscosity, pumpable solutions (or melt) at concentrations as high as 70-100%, which allows them to be easily handled in the manufacturing plant. The surfactants herein also have the advantage of providing a lower sudsing profile than the N-methyl polyhydroxy fatty acid amides, which desirably decreases the carry-over of suds into the rinse bath. The combined attributes of ease-of-formulation and better, low suds profile is an additional advantage for these surfactants. In addition, the surfactants herein can be

exhibit improved solubility in water over the corresponding N-alkyl polyhydroxy fatty acid amide surfactants, even at low temperatures (5°-30°C). The high solubility of the surfactants herein allows them to be formulated as highly concentrated liquid detergents. Moreover, the surfactants herein can be easily prepared as low viscosity, pumpable solutions (or melt) at concentrations as high as 70-100%, which allows them to be easily handled in the manufacturing plant. The surfactants herein also have the advantage of providing a lower sudsing profile than the N-methyl polyhydroxy fatty acid amides, which desirably decreases the carry-over of suds into the rinse bath. The combined attributes of ease-of-formulation and better, low suds profile is an additional advantage for these surfactants. In addition, the surfactants herein can be produced from renewable resources such as fats and sugars, rather than from petrochemicals, and are biodegradable. These and other benefits are secured by the present invention.

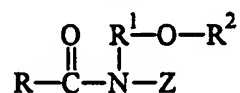
BACKGROUND ART

Japanese Kokai HEI 3[1991]-246265 Osamu Tachizawa, U.S. Patents 5,194,639, 5,174,927 and 5,188,769 and WO 9,206,171, 9,206,151, 9,206,150 and 9,205,764 relate to various polyhydroxy fatty acid amide surfactants and uses thereof.

SUMMARY OF THE INVENTION

The present invention encompasses liquid laundry detergents which can be in dilute form, i.e., containing less than about 25% of total surfactants, typically 10%-20% surfactants, or in concentrated form, i.e., containing at least about 25% by weight of total surfactants, and typically comprising from about 25% to about 50% by weight of total surfactants, with a desirable, highly concentrated form preferably having a viscosity no greater than about 800 cps, and comprising:

(a) an amide surfactant of the formula



wherein R is a C₇-C₂₁ hydrocarbyl moiety, R¹ is a C₂-C₈ hydrocarbyl moiety, R² is a C₁-C₈ hydrocarbyl or oxy-hydrocarbyl moiety, and Z is a polyhydroxy hydrocarbyl unit having a linear chain with at least two hydroxyls directly connected to the chain;

- (b) one or more anionic surfactants;
- (c) optional deterative adjuncts; and
- (d) a fluid carrier.

Preferred liquid compositions herein are those wherein R¹ is a linear or branched C₂-C₄ alkylene moiety and R² is a linear or branched C₁-C₄ alkyl moiety,

and especially wherein substituent $-R^1-O-R^2$ is a member selected from the group consisting of 2-methoxyethyl and 3-methoxypropyl, and wherein R is C_{11} . The palm fatty acid material provides excellent low sudsing. In the above formula, Z is a substituent which is preferably derived from a member selected from the group consisting of glucose, fructose, maltose, lactose, xylose and glycerol moieties, and mixtures thereof.

The invention also encompasses fully-formulated detergent compositions which may additionally comprise a deterative adjunct ingredient which is a member selected from the group consisting of enzymes, builders, bleaches, soil release agents, auxiliary surfactants, and mixtures thereof.

The invention herein thus provides a method for cleaning substrates, comprising contacting said substrates with a composition as described above in the presence of water. Typical usage levels range from about 100 ppm to about 10,000 ppm in water. The method is especially useful for laundering fabrics.

All percentages, ratios and proportions herein are by weight. All documents cited are incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The N-alkoxy and N-aryloxy polyhydroxy fatty acid amide surfactants used in the practice of this invention are quite different from traditional ethoxylated nonionics, due to the use of a linear polyhydroxy chain as the hydrophilic group instead of the ethoxylation chain. Conventional ethoxylated nonionic surfactants have cloud points with the less hydrophilic ether linkages. They become less soluble, more surface active and better performing as temperature increases, due to thermally induced randomness of the ethoxylation chain. When the temperature gets lower, ethoxylated nonionics become more soluble by forming micelles at very low concentration and are less surface active, and lower performing, especially when washing time is short.

In contrast, the polyhydroxy fatty acid amide surfactants have polyhydroxyl groups which are strongly hydrated and do not exhibit cloud point behavior. It has been discovered that they exhibit Krafft point behavior with increasing temperature and thus higher solubility at elevated temperatures. They also have critical micelle concentrations similar to anionic surfactants, and it has been surprisingly discovered that they clean like anionics.

Moreover, the polyhydroxy fatty acid amides herein are different from the alkyl polyglycosides (APG) which comprise another class of polyhydroxyl nonionic surfactants. While not intending to be limited by theory, it is believed that the

difference is in the linear polyhydroxyl chain of the polyhydroxy fatty acid amides vs. the cyclic APG chain which prevents close packing at interfaces for effective cleaning.

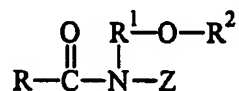
With respect to the N-alkoxy and N-aryloxy polyhydroxy fatty acid amides, such surfactants have now been found to have a much wider temperature usage profile than their N-alkyl counterparts, and they require no or little cosurfactants for solubility at temperatures as low as 5°C. Such surfactants also provide easier processing due to their lower melting points. It has now further been discovered that these surfactants are biodegradable.

As is well-known to formulators, most laundry detergents are formulated with mainly anionic surfactants, with nonionics sometimes being used for grease/oil removal. Since it is well known that nonionic surfactants are far better for enzymes, polymers, soil suspension and skin mildness, it would be preferred that laundry detergents use more nonionic surfactants. Unfortunately, traditional nonionics do not clean well enough in cooler water with short washing times.

It has now also been discovered that the N-alkoxy and N-aryloxy polyhydroxy fatty acid amide surfactants herein provide additional benefits over conventional nonionics, as follows:

- a. Much enhanced stability and effectiveness of new enzymes, like cellulase and lipase, and improved performance of soil release polymers;
- b. Much less dye bleeding from colored fabrics, with less dye transfer onto whites;
- c. Better water hardness tolerance;
- d. Better greasy soil suspension with less redeposition onto fabrics;
- e. The ability to incorporate higher levels of surfactants not only into Heavy Duty Liquid Detergents (HDL's), but also into Heavy Duty Granules (HDG's) with the new solid surfactants herein; and
- f. The ability to formulate stable, high performance "All-Nonionic" or "High Nonionic/Low Anionic" HDL and HDG compositions.

The N-alkoxy and N-aryloxy polyhydroxy fatty acid amide surfactants used herein comprise amides of the formula:



wherein: R is C₇-C₂₁ hydrocarbyl, preferably C₉-C₁₇ hydrocarbyl, including straight-chain (preferred), branched-chain alkyl and alkenyl, as well as substituted alkyl and alkenyl, e.g., 12-hydroxyoleic, or mixtures thereof; R¹ is C₂-C₈ hydrocarbyl including straight-chain, branched-chain and cyclic (including aryl), and is

preferably C₂-C₄ alkylene, i.e., -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂- and -CH₂(CH₂)₂CH₂-; and R² is C₁-C₈ straight-chain, branched-chain and cyclic hydrocarbyl including aryl and oxy-hydrocarbyl, and is preferably C₁-C₄ alkyl or phenyl; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH₂-(CHOH)_n-CH₂OH, -CH(CH₂OH)-(CHOH)_{n-1}-CH₂OH, -CH₂-(CHOH)₂(CHOR')(CHOH)-CH₂OH, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or poly- saccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly -CH₂-(CHOH)₄-CH₂OH.

In compounds of the above formula, nonlimiting examples of the amine substituent group -R¹-O-R² can be, for example: 2-methoxyethyl-, 3-methoxypropyl-, 4-methoxybutyl-, 5-methoxypentyl-, 6-methoxyhexyl-, 2-ethoxyethyl-, 3-ethoxypropyl-, 2-methoxypropyl, methoxybenzyl-, 2-isopropoxyethyl-, 3-isopropoxypropyl-, 2-(t-butoxy)ethyl-, 3-(t-butoxy)propyl-, 2-(isobutoxy)ethyl-, 3-(isobutoxy)propyl-, 3-butoxypropyl, 2-butoxyethyl, 2-phenoxyethyl-, methoxycyclohexyl-, methoxycyclohexylmethyl-, tetrahydrofurfuryl-, tetrahydropyranyloxyethyl-, 3-[2-methoxyethoxy]propyl-, 2-[2-methoxyethoxy]ethyl-, 3-[3-methoxypropoxy]propyl-, 2-[3-methoxypropoxy] ethyl-, 3-[methoxypolyethyleneoxy]propyl-, 3-[4-methoxybutoxy]propyl-, 3-[2-methoxyisopropoxy]propyl-, $\text{CH}_3\text{O}-\text{CH}_2-\text{CH}(\text{CH}_3)-$ and $\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)\text{CH}_2-\text{O}-(\text{CH}_2)_3-$.

R-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, ricinolamide, etc.

While the synthesis of N-alkoxy or N-aryloxy polyhydroxy fatty acid amides can prospectively be conducted using various processes, contamination with cyclized by-products and other colored materials may be problematic. As an overall proposition, the synthesis method for these surfactants comprises reacting the

appropriate N-alkoxy or N-aryloxy-substituted aminopolyols with, preferably, fatty acid methyl esters in a solvent using an alkoxide catalyst (e.g., sodium methoxide or the sodium salts of glycerin or propylene glycol) at temperatures of about 85°C to provide products having desirable low levels (preferably, less than about 10%) of cyclized by-products and also with improved color and improved color stability, e.g., Gardner Colors below about 4, preferably between 0 and 2. If desired, any unreacted N-alkoxy or N-aryloxy amino polyol remaining in the product can be acylated with an acid anhydride, e.g., acetic anhydride, maleic anhydride, or the like, in water at 50°C-85°C to minimize the overall level of such residual amines in the product. Residual sources of straight-chain primary fatty acids, which can suppress suds, can be depleted by reaction with, for example, monoethanolamine at 50°C-85°C.

If desired, the water solubility of the solid N-alkoxy polyhydroxy fatty acid amide surfactants herein can be enhanced by quick cooling from a melt. While not intending to be limited by theory, it appears that such quick cooling re-solidifies the melt into a metastable solid which is more soluble in water than the pure crystalline form of the N-alkoxy polyhydroxy fatty acid amide. Such quick cooling can be accomplished by any convenient means, such as by use of chilled (0°C-10°C) rollers, by casting the melt onto a chilled surface such as a chilled steel plate, by means of refrigerant coils immersed in the melt, or the like.

By "cyclized by-products" herein is meant the undesirable reaction by-products of the primary reaction wherein it appears that the multiple hydroxyl groups in the polyhydroxy fatty acid amides can form ring structures. It will be appreciated by those skilled in the chemical arts that the preparation of the polyhydroxy fatty acid amides herein using the di- and higher saccharides such as maltose will result in the formation of polyhydroxy fatty acid amides wherein linear substituent Z (which contains multiple hydroxy substituents) is naturally "capped" by a polyhydroxy ring structure. Such materials are not cyclized by-products, as defined herein.

The following illustrates the synthesis in more detail.

EXAMPLE I

Preparation of N-(2-methoxyethyl)glucamine

N-(2-methoxyethyl)glucosylamine (sugar adduct) is prepared starting with 1728.26 g of 50 wt.% 2-methoxyethylamine in water (11.5 moles, 1.1 mole equivalent of 2-methoxyethylamine) placed under an N₂ blanket at 10°C. 2768.57 grams of 50 wt.% glucose in water (10.46 moles, 1 mole equivalent of glucose), which is degassed with N₂, is added slowly, with mixing, to the methoxyethylamine solution keeping the temperature below 10°C. The solution is mixed for about 40

minutes after glucose addition is complete. It can be used immediately or stored 0°C-5°C for several days.

About 278 g (~15 wt.% based on amount of glucose used) of Raney Ni (Activated Metals & Chemicals, Inc. product A-5000) is loaded into a 2 gallon reactor (316 stainless steel baffled autoclave with DISPERSIMAX hollow shaft multi-blade impeller) with 4L of water. The reactor is heated, with stirring, to 130°C at about 1500 psig hydrogen for 30 minutes. The reactor is then cooled to room temperature and the water removed to 10% of the reactor volume under hydrogen pressure using an internal dip tube.

The reactor is vented and the sugar adduct is loaded into the reactor at ambient hydrogen pressure. The reactor is then purged twice with hydrogen. Stirring is begun, the reactor is heated to 50°C, pressurized to about 1200 psig hydrogen and these conditions are held for about 2 hours. The temperature is then raised to 60°C for 10 minutes, 70°C for 5 minutes, 80°C for 5 minutes, 90°C for 10 minutes, and finally 100°C for 25 minutes.

The reactor is then cooled to 50°C and the reaction solution is removed from the reactor under hydrogen pressure via an internal dip tube and through a filter in closed communication with the reactor. Filtering product under hydrogen pressure allows removal of any nickel particles without nickel dissolution.

Solid N-(2-methoxyethyl)glucamine is recovered by evaporation of water and excess 2-methoxyethylamine. The product purity is approximately 90% by G.C. Sorbitol is the major impurity at about 10%. The N-(2-methoxyethyl)glucamine can be used as is or purified to greater than 99% by recrystallization from methanol.

EXAMPLE II

Preparation of C₁₂-N-(2-Methoxyethyl)glucamide

N-(2-methoxyethyl)glucamine, 1195 g (5.0 mole; prepared according to Example I) is melted at 135°C under nitrogen. A vacuum is pulled to 30 inches (762 mm) Hg for 15 minutes to remove gases and moisture. Propylene glycol, 21.1 g (0.28 mole) and fatty acid methyl ester (Procter & Gamble CE 1295 methyl ester) 1097 (5.1 mole) are added to the preheated amine. Immediately following, 25% sodium methoxide, 54 g (0.25 mole) is added in halves.

Reactants weight: 2367.1 g

Theoretical MeOH generated: $(5.0 \times 32) + (0.75 \times 54) + (0.24 \times 32) = 208.5 \text{ g}$

Theory product: FW 422 2110 g 5.0 mole

The reaction mixture is homogeneous within 2 minutes of adding the catalyst. It is cooled with warm H₂O to 85°C and allowed to reflux in a 5-liter, 4-neck round bottom flask equipped with a heating mantle, Trubore stirrer with Teflon paddle, gas inlet and outlet, Thermowatch, condenser, and air drive motor. When catalyst is added, time = 0. At 60 minutes, a GC sample is taken and a vacuum of 7 inches (178 mm) Hg is started to remove methanol. At 120 minutes, another GC sample is taken and the vacuum has been increased to 10 inches (254 mm) Hg. At 180 minutes, another GC sample is taken and the vacuum has been increased to 16 inches (406 mm) Hg. After 180 minutes at 85°C, the remaining weight of methanol in the reaction is 4.1% based on the following calculation: $2251 \text{ g current reaction wt.} - (2367.1 \text{ g reactants wt.} - 208.5 \text{ g theoretical MeOH}) / 2251 \text{ g} = 4.1\% \text{ MeOH}$ remaining in the reaction. After 180 minutes, the reaction is bottled and allowed to solidify at least overnight to yield the desired product.

EXAMPLE III

Preparation of N-(3-methoxypropyl)glucamine

About 300 g (about 15 wt.% based on amount of glucose used) of Raney Ni (Activated Metals & Chemicals, Inc. product A-5000 or A-5200) is contained in a 2 gallon reactor (316 stainless steel baffled autoclave with DISPERSIMAX hollow shaft multi-blade impeller) pressurized to about 300 psig with hydrogen at room temperature. The nickel bed is covered with water taking up about 10% of the reactor volume.

1764.8 g (19.8 moles, 1.78 mole equivalent) of 3-methoxypropylamine (99%) is maintained in a separate reservoir which is in closed communication with the reactor. The reservoir is pressurized to about 100 psig with nitrogen. 4000 g of 50 wt.% glucose in water (11.1 moles, 1 mole equivalent of glucose) is maintained in a second separate reservoir which is also in closed communication with the reactor and is also pressurized to about 100 psig with nitrogen.

The 3-methoxypropylamine is loaded into the reactor from the reservoir using a high pressure pump. Once all the 3-methoxypropylamine is loaded into the reactor, stirring is begun and the reactor heated to 60°C and pressurized to about 800 psig hydrogen. The reactor is stirred at 60°C and about 800 psig hydrogen for about 1 hour.

The glucose solution is then loaded into the reactor from the reservoir using a high pressure pump similar to the amine pump above. However, the pumping rate on the glucose pump can be varied and on this particular run, it is set to load the glucose in about 1 hour. Once all the glucose has been loaded into the reactor, the pressure is

boosted to about 1500 psig hydrogen and the temperature maintained at 60°C for about 1 hour. The temperature is then raised to 70°C for 10 minutes, 80°C for 5 minutes, 90°C for 5 minutes, and finally 100°C for 15 minutes.

The reactor is then cooled to 60°C and the reaction solution is removed from the reactor under hydrogen pressure via an internal dip tube and through a filter in closed communication with the reactor. Filtering under hydrogen pressure allows removal of any nickel particles without nickel dissolution.

Solid N-(3-methoxypropyl)glucamine is recovered by evaporation of water and excess 3-methoxypropylamine. The product purity is approximately 90% by G.C. Sorbitol is the major impurity at about 3%. The N-(3-methoxypropyl)glucamine can be used as is or purified to greater than 99% by recrystallization from methanol.

EXAMPLE IV

Preparation of C₁₂-N-(3-Methoxypropyl)glucamide

N-(3-methoxypropyl)glucamine, 1265 g (5.0 mole prepared according to Example III) is melted at 140°C under nitrogen. A vacuum is pulled to 25 inches (635 mm) Hg for 10 minutes to remove gases and moisture. Propylene glycol, 109 g (1.43 mole) and CE 1295 methyl ester, 1097 (5.1 mole) are added to the preheated amine. Immediately following, 25% sodium methoxide, 54 g (0.25 mole) is added in halves.

Reactants weight: 2525 g

Theoretical MeOH generated: $(5.0 \times 32) + (0.75 \times 54) + (0.24 \times 32) = 208.5 \text{ g}$

Theory product: FW 436 2180 g 5.0 mole

The reaction mixture is homogeneous within 1 minute of adding the catalyst. It is cooled with warm H₂O to 85°C and allowed to reflux in a 5-liter, 4-neck round bottom flask equipped with a heating mantle, Trubore stirrer with Teflon paddle, gas inlet and outlet, Thermowatch, condenser, and air drive motor. When catalyst is added, time = 0. At 60 minutes, a GC sample is taken and a vacuum of 7 inches (178 mm) Hg is started to remove methanol. At 120 minutes, another GC sample is taken and the vacuum has been increased to 12 inches (305 mm) Hg. At 180 minutes, another GC sample is taken and the vacuum has been increased to 20 inches (508 mm) Hg. After 180 minutes at 85°C, the remaining weight of methanol in the reaction is 2.9% based on the following calculation: $2386 \text{ g current reaction wt.} - (2525 \text{ g reactants wt.} - 208.5 \text{ g theoretical MeOH}) / 2386 \text{ g} = 2.9\% \text{ MeOH remaining in the reaction.}$ After 180 minutes, the reaction is bottled and allowed to solidify at least overnight to yield the desired product.

EXAMPLE V

C₁₈ Methoxypropyl Glucose Amide - N-3-(methoxypropyl)glucamine, 40 g (0.158 mole) is melted at 145°C under nitrogen. A vacuum is applied to 38.1 cm (15 inches) Hg for 5 minutes to remove gases and moisture. Separately, methylstearate, 5 47.19 g (0.158 mole) is preheated to 130°C and added to the melted amine with rapid stirring along with 9.0 grams of propylene glycol (10 weight % based on reactants). Immediately following, 25% sodium methoxide, 1.7 g (0.0079 mole) is added.

The reaction mixture is homogeneous within 2 minutes of adding the catalyst at 130°C. It is allowed to reflux in order to cool to 85-90°C in a 250 ml, 3 neck 10 round bottom flask equipped with a hot oil bath, TRUBORE stirrer with TEFLON paddle, gas inlet and outlet, THERMOWATCH, condenser, and stirrer motor. The reaction requires about 35 minutes to reach 90°C. After 3 hours at 85-90°C a vacuum is applied to remove methanol. The reaction mixture is poured out into a jar after a total of 4 hours. The solid reaction product is recrystallized from 400 mls of 15 acetone and 20 mls of methanol. The filter cake is washed twice with 100 ml portions of acetone and is dried in a vacuum oven. A second recrystallization is performed on 51.91 grams of the product of the first recrystallization using 500 mls acetone and 50 mls methanol to give after filtration, washing with two 100 ml portions of acetone and drying in a vacuum oven a yield of 47.7 grams of the N-octadecanoyl-N-(3- 20 methoxypropyl)glucamine. Melting point of the sample is 80°C-89°C. If desired, the product can be further purified using an acetone/methanol solvent.

EXAMPLE VI

C₁₆ Methoxypropyl Glucose Amide - The reaction of Example V is repeated using an equivalent amount of methyl palmitate to replace the methyl stearate. The 25 resulting hexadecanoyl-N-(3-methoxypropyl)glucamine has a melting point of 84°C. If desired, the product can be further purified using an acetone/methanol solvent.

EXAMPLE VII

Mixed Palm Fatty Acid Methoxypropyl Glucose Amide - N-(3-methoxypropyl)glucamine, 1265 g (5.0 mole) is melted at 145°C under nitrogen. A 30 vacuum is applied to 38.1 cm (15 inches) Hg for 10 minutes to remove gases and moisture. Separately, hardened palm stearine methyl ester, 1375 g (5.0 mole) is preheated to 130°C and added to the melted amine with rapid stirring. Immediately following, 25% sodium methoxide, 54 g (0.25 mole) is added through a dropping funnel. Half the catalyst is added before the reaction is homogeneous to control the 35 hard reflux of methanol. After homogeneity is reached, the other half of the catalyst is added within 10 minutes.

Reactants weight: 2694 g

Theoretical MeOH generated: $(5.0 \times 32) + (0.75 \times 54) + (0.25 \times 32) = 208.5$ g MeOH

Theory product: FW 496 2480 g 5.0 mole

5 The reaction mixture is homogeneous within 5 minutes of adding the first half of the catalyst at 132°C. It is allowed to reflux in order to cool to 90-95°C in a 5 liter, 4 neck round bottom flask equipped with a heating mantle, TRUBORE stirrer with TEFLON paddle, gas inlet and outlet, THERMOWATCH, condenser, and air drive motor. When the first half of the catalyst is added, time = 0. At 40 minutes, a vacuum of 25.4 cm (10 inches) Hg is applied to remove methanol. At 48 minutes, vacuum is increased to 43.2 cm (17 inches) Hg. At 65 minutes, the remaining weight of methanol in the reaction is 2.9% based on the following calculation:

2559 g current reaction wt - (2694 g reactants wt - 208.5 g theoretical MeOH)/2559 g = 2.9% MeOH remaining in the reaction.

15 By 120 minutes, the vacuum has been increased to 50.8 cm (20 inches) Hg. At 180 minutes, the vacuum has been increased to 58.4 cm (23 inches) Hg and the reaction is poured into a stainless pan and allowed to solidify at room temperature. Also, the remaining weight of methanol is calculated to be 1.3%. After sitting for 4 days, it is hand ground for use.

20 In an economical process, fatty glyceride esters can also be used in the foregoing process. Natural plant oils such as palm, palm kernel oil, soy and canola, as well as tallow are typical sources for such materials. Thus, for example, in an alternate mode, the above process is conducted using palm kernel oil to provide the desired mixture of N-alkoxyglucamine surfactants.

25 In the general manner of Example IV (with methanol solvent) or V, oleoyl-N-(3-methoxypropyl)glucamine is prepared by reacting 49.98 grams of N-(3-methoxypropyl)glucamine with 61.43 g of methyl oleate in the presence of 4.26 g of 25 wt% NaOCH₃. The oleoyl derivative of N-(2-methoxyethyl) glucamine is prepared in like manner. The corresponding palm kernel oil-derived amides are prepared in like manner.

Glyceride Process

If desired, the N-alkoxy and N-aryloxy surfactants used herein may be made directly from natural fats and oils rather than fatty acid methyl esters. This so-called "glyceride process" results in a product which is substantially free of conventional fatty acids such as lauric, myristic and the like, which are capable of precipitating as

calcium soaps under wash conditions, thus resulting in unwanted residues on fabrics or filming/spotting in, for example, hard surface cleaners and dishware cleaners.

Triglyceride Reactant - The reactant used in the glyceride process can be any of the well-known fats and oils, such as those conventionally used as foodstuffs or as fatty acid sources. Non-limiting examples include: CRISCO oil; palm oil; palm kernel oil; corn oil; cottonseed oil; soybean oil; tallow; lard; canola oil; rapeseed oil; peanut oil; tung oil; olive oil; menhaden oil; coconut oil; castor oil; sunflower seed oil; and the corresponding "hardened", i.e., hydrogenated oils. If desired, low molecular weight or volatile materials can be removed from the oils by steam-stripping, vacuum stripping, treatment with carbon or "bleaching earths" (diatomaceous earth), or cold tempering to further minimize the presence of malodorous by-products in the surfactants prepared by the glyceride process.

N-substituted Polyhydroxy Amine Reactant - The N-alkyl, N-alkoxy or N-aryloxy polyhydroxy amines used in the process are commercially available, or can be prepared by reacting the corresponding N-substituted amine with a reducing sugar, typically in the presence of hydrogen and a nickel catalyst as disclosed in the art. Non-limiting examples of such materials include: N-(3-methoxypropyl) glucamine; N-(2-methoxyethyl) glucamine; and the like.

Catalyst - The preferred catalysts for use in the glyceride process are the alkali metal salts of polyhydroxy alcohols having at least two hydroxyl groups. The sodium (preferred), potassium or lithium salts may be used. The alkali metal salts of monohydric alcohols (e.g., sodium methoxide, sodium ethoxide, etc.) could be used, but are not preferred because of the formation of malodorous short-chain methyl esters, and the like. Rather, it has been found to be advantageous to use the alkali metal salts of polyhydroxy alcohols to avoid such problems. Typical, non-limiting examples of such catalysts include sodium glycolate, sodium glycerate and propylene glycolates such as sodium propyleneglycolate (both 1,3- and 1,2-glycolates can be used; the 1,2-isomer is preferred), and 2-methyl-1,3-propyleneglycolate. Sodium salts of NEODOL-type ethoxylated alcohols can also be used.

Reaction Medium - The glyceride process is preferably not conducted in the presence of a monohydric alcohol solvent such as methanol, because malodorous acid esters may form. However, it is preferred to conduct the reaction in the presence of a material such as an alkoxylated alcohol or alkoxylated alkyl phenol of the surfactant type which acts as a phase transfer agent to provide a substantially homogeneous reaction mixture of the polyhydroxy amine and oil (triglyceride) reactants. Typical examples of such materials include: NEODOL 10-8, NEODOL 23-3, NEODOL 25-

12 AND NEODOL 11-9. Pre-formed quantities of the N-alkoxy and N-aryloxy polyhydroxy fatty acid amides, themselves, can also be used for this purpose. In a typical mode, the reaction medium will comprise from about 10% to about 25% by weight of the total reactants.

- 5 Reaction Conditions - The glyceride process is preferably conducted in the melt. N-substituted polyhydroxy amine, the phase transfer agent (preferred NEODOL) and any desired glyceride oil are co-melted at 120°C-140°C under vacuum for about 30 minutes. The catalyst (preferably, sodium propylene glycolate) at about 5 mole % relative to the polyhydroxy amine is added to the reaction mixture.
- 10 The reaction quickly becomes homogeneous. The reaction mixture is immediately cooled to about 85°C. At this point, the reaction is nearly complete. The reaction mixture is held under vacuum for an additional hour and is substantially complete at this point.

- 15 In an alternate mode, the NEODOL, oil, catalyst and polyhydroxy amine are mixed at room temperature. The mixture is heated to 85°C-90°C, under vacuum. The reaction becomes clear (homogeneous) in about 75 minutes. The reaction mixture is maintained at about 90°C, under vacuum, for an additional two hours. At this point the reaction is complete.

- 20 In the glyceride process, the mole ratio of triglyceride oil:polyhydroxy amine is typically in the range of about 1:2 to 1:3.1.

Product Work-Up: The product of the glyceride process will contain the polyhydroxy fatty acid amide surfactant and glycerol. The glycerol may be removed by distillation, if desired. If desired, the water solubility of the solid polyhydroxy fatty acid amide surfactants can be enhanced by quick cooling from a melt, as noted above.

- 25 Anionic Surfactants - The compositions herein contain various anionic surfactants. Such surfactants are typically present at levels of from about 5% to about 50% of the compositions.

- Nonlimiting examples of surfactants useful herein include the conventional C₁₁-C₁₈ alkyl benzene sulfonates and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates, the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻ M⁺) CH₃ and CH₃ (CH₂)_y(CHOSO₃⁻ M⁺) CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9; and M is a water-solubilizing cation, especially sodium, the C₁₀-C₁₈ alkyl alkoxy sulfates (especially EO 1-5 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the sulfated C₁₀-C₁₈ alkyl polyglycosides, C₁₂-C₁₈ alpha-sulfonated fatty acid esters, C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"),
- 30
- 35

and the like. Other conventional useful surfactants are listed in standard texts. If desired, C₁₂-C₁₈ alcohol and C₆-C₁₂ alkyl phenol ethoxylates and C₁₀-C₁₈ amine oxides can also be used in conjunction with the aforesaid anionic surfactants.

Fluid Carrier - Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols such as methanol, ethanol or iso-propanol are preferred for solubilizing detergent ingredients, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. While the fluid carrier typically contains some water, anhydrous carriers may also be employed. Thus, for example, the compositions herein can comprise the N-methoxypropyl polyhydroxy fatty acid amide surfactant dissolved in a liquid (room temperature) ethoxylated alcohol surfactant plus 1,2-propane diol as the liquid carrier, and remain fully stable and soluble on storage without the need for water or other solubilizing agents. The compositions may contain from 5% to 90%, typically 10% to 50% of fluid carriers.

Adjunct Ingredients

The compositions herein can optionally include one or more other detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition (e.g., perfumes, colorants, dyes, etc.). The following are illustrative examples of such adjunct materials.

Builders - Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

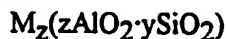
Inorganic detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates),

phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders. Moreover, the secondary (2,3) alkyl sulfate plus enzyme components perform best in the presence of weak, nonphosphate builders which allow free calcium ions to be present. This is especially true for liquid compositions.

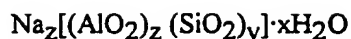
Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders can be used in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



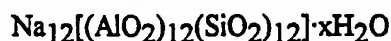
wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2; and y is 1; this material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO_3 hardness per gram of anhydrous aluminosilicate. Preferred aluminosilicates are zeolite builders which have the formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available.

5 These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite
10 A, Zeolite P (B), and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Preferably, the aluminosilicate has a particle size of about 0.1-10
15 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be
20 added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses
25 the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents
30 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergent builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as
35 ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates

such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Oxydisuccinate builders are also useful in such compositions.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Enzymes - Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their

choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

5 Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1%, by weight of a commercial enzyme preparation. Protease enzymes are usually present in such
10 commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B.subtilis* and *B.licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range
15 of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S
20 (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985).

25 Amylases include, for example, α -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable
30 cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-
35 A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53-20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 4,261,868, issued April 14, 1981 to Horn, et al, U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319, and 3,519,570.

Enzyme Stabilizers - The enzymes employed herein are stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. 4,537,706, cited above. Typical detergents, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In some detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from about 0.05% to about 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although

other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

5 Bleaching Compounds - Bleaching Agents and Bleach Activators - The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially
10 for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

 The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning
15 purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

 One category of bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents
20 include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydo-decanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published
25 February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

 Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching
30 compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

 Mixtures of bleaching agents can also be used.

35 Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in

aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonated zinc phthalocyanine.

Polymeric Soil Release Agent - Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C₃

oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C₃ oxyalkylene terephthalate units is about 2:1 or lower, (ii) C₄-C₆ alkylene or oxy C₄-C₆ alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably
5 poly(vinyl acetate), having a degree of polymerization of at least 2, or (iv) C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C₁-C₄ alkyl ether and/or C₄
10 hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of
15 polymerization of from 2 to about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C₄-C₆ alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as $\text{MO}_3\text{S}(\text{CH}_2)_n\text{OCH}_2\text{CH}_2\text{O}-$, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to
20 Gosselink.

Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially
25 available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C₁-C₄ alkyl and C₄ hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments
30 include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West
35 Germany).

One type of useful soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

Another useful polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units containing 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Another useful polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J. J. Scheibel and E. P. Gosselink.

Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Other polymeric soil release agents include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexaacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates), nitrilotris (methylenephosphonates) and diethylenetriamine-pentakis (methylenephosphonates) as DEQUEST. Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents - The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and anti-redeposition properties. Liquid detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylated amines.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal/antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European

Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the
5 carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates
10 and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

15 Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic
20 acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic
25 acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal,
30 ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble
35 salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000,

more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal/antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, alone or in conjunction with zeolite builders.

Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Arctic White CC and Arctic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)biphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl-amino coumarin; 1,2-bis(-benzimidazol-2-yl)-ethylene; 1,3-diphenylphrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho-[1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance under conditions such as those found in European-style front loading laundry washing machines, or in the concentrated detergent process of U.S. Patents 4,489,455 and 4,489,574, or when the detergent compositions herein optionally include a relatively high sudsing adjunct surfactant.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acids and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g. K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 5°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin,"

as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units of SiO_2 units in a ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and
- (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel;

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), and not polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a

primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine.

Suds suppressors, when utilized, are preferably present in a "suds suppressing amount." By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

In addition to the foregoing ingredients, the compositions herein can also be used with a variety of other adjunct ingredients which provide still other benefits in various compositions within the scope of this invention. The following illustrates a variety of such adjunct ingredients, but is not intended to be limiting therein.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners, as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents

can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to
5 remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexaacetates,
10 diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis
15 (methylenephosphonates), nitrilotris (methylenephosphonates) and diethylenetriaminepentakis (methylenephosphonates) as DEQUEST. Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the
20 compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), as described in U.S. Patent 4,704,233, November 3, 1987, to
25 Hartman and Perkins.

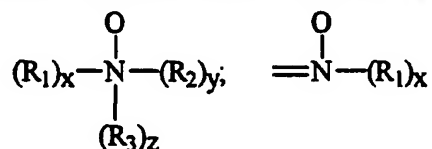
If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Dye Transfer Inhibiting Agents - The compositions of the present
30 invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically
35

comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $pK_a < 10$, preferably $pK_a < 7$, more preferred $pK_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

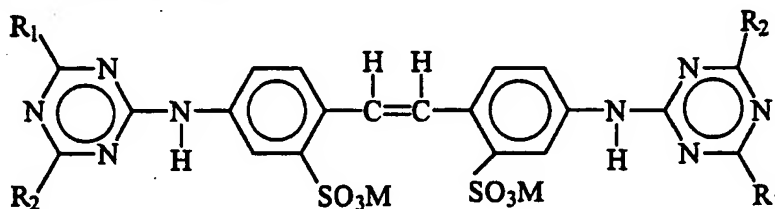
The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂

is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

5 Other Ingredients - A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10%
10 levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble salts such as CaCl₂, CaSO₄, MgCl₂, MgSO₄, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional sudsing and to enhance
15 grease removal performance.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the
20 porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃₋₁₅ ethoxylated alcohol EO(7) nonionic surfactant.
25 Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the
30 aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between
35 about 7.0 and about 9-10, preferably between about 7.5 and about 9.5. Techniques

for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

The following are typical, nonlimiting examples which illustrate the detergent compositions and uses of the present invention. Preferred compositions for most purposes contain no phosphates.

The liquid laundry detergent of Example I is prepared by dissolving or dispersing the indicated ingredients in an aqueous carrier and adjusting the pH in the preferred range of 7.5-9.0.

EXAMPLE VIII

A liquid laundry detergent composition herein comprises the following.

<u>Ingredient</u>	<u>% (wt.)</u>
Secondary (2,3) alkyl sulfate*	15.0
C ₁₂ -N-(3-methoxypropyl) glucamide	5.0
Sodium citrate	3.0
C ₁₀ alcohol ethoxylate (3)	13.0
Monoethanolamine	2.5
MAXATASE (enzyme)	0.5
LIPOLASE (enzyme)	0.5
CaCl ₂	0.9
Water/propylene glycol/ethanol (100:1:1)	Balance

*C₁₂-C₁₆ average chain length; Na salt form; less than 1% Na₂SO₄.

EXAMPLE IX

A liquid laundry detergent composition suitable for use at the relatively high concentrations common to front-loading automatic washing machines, especially in Europe, and over a wide range of temperatures is as follows.

<u>Ingredient</u>	<u>Weight %</u>
C ₁₄₋₁₆ -N-(3-methoxypropyl) glucamide	10.0
C ₁₄₋₁₅ -EO(2.25) sulfate, Na salt	10.0
C ₁₄₋₁₅ -EO(7)	4.0
C ₁₂₋₁₄ alkenylsuccinic anhydride ¹	4.0
C ₁₂₋₁₄ fatty acid*	3.0
Citric acid (anhydrous)	4.6
Protease (enzyme) ²	0.37
Termamyl (enzyme) ³	0.12
Lipolase (enzyme) ⁴	0.36
Carezyme (enzyme) ⁵	0.12

	EDDS ⁶	1.0
	NaOH (pH to 7.6)	5.5
	1,2 propanediol	4.7
	Ethanol	4.0
5	Sodium metaborate	4.0
	CaCl ₂	0.014
	Ethoxylated tetraethylene pentamine ⁷	0.4
	Brightener ⁸	0.13
	Silane ⁹	0.04
10	Soil release polymer ¹⁰	0.2
	Silicone (suds control) ¹¹	0.4
	Silicone dispersant ¹²	0.2
	Water and minors	Balance

¹As SYNPRAX 3 from ICI or DTSA from Monsanto.

15 ²As Protease B as described in EPO 0342177 November 15, 1989,
percentage at 40 g/l.

³Amylase, from NOVO; percentage at 300 KNU/g.

⁴Lipase, from NOVO; percentage at 100 KLU/g.

⁵Cellulase from NOVO; percentage at 5000 CEVU/l.

20 ⁶Ethylenediamine disuccinate.

⁷From BASF as LUTENSOL P6105.

⁸BLANKOPHOR CPG766, Bayer.

⁹Silane corrosion inhibitor, available as A1130 from Union Carbide or
DYNASYLAN TRIAMINO from HOIs.

25 ¹⁰Polyester, per U.S. Patent 4,711,730.

¹¹Silicone suds control agent available as Q2-3302 from Dow Corning.

¹²Dispersant for silicone suds control agent available as DC-3225C from
Dow Corning.

30 *Preferred fatty acid is topped palm kernel, comprising 12% oleic acid and
2% each of stearic and linoleic.

EXAMPLE X

Highly concentrated liquid laundry detergents are as follows.

<u>Ingredient</u>	<u>C₁₂ N-methoxy- propyl)glucamide</u>	<u>C_{16/18} N-(3-meth- oxypropyl)glucamide</u>
	<u>% (wt.)</u>	<u>% (wt.)</u>
C ₁₄₋₁₅ EO(2.25) sulfate, Na	31.46	31.21
5 Glucamide surfactant	10.50	10.40
Citric acid	—	0.19
C ₁₂₋₁₄ fatty acid	4.00	4.00
Ethoxylated tetraethylene pentamine	1.00	0.99
10 Boric acid	2.00	2.00
NaOH	3.85	3.79
1,2-propanediol	10.00	9.15
Ethanol	7.00	6.55
Monoethanolamine	1.06	1.05
15 Sodium cumene sulfonate	4.00	3.96
H ₂ O/minors	25.13	26.74
pH 10% aq. solution	8.00	8.29
Viscosity*	580	880

*Brookfield DVII viscometer, 60 rpms, spindle 2.

- 20 The foregoing composition is designed for use at the 0.25 cup (59 mls) level in a conventional U.S. washine machine, or its equivalent. By contrast, the viscosity of an equivalent liquid product comprising a coconutalky N-methyl glucamide surfactant is above 100,000, i.e., a gel.

EXAMPLE XI

- 25 A liquid laundry detergent with improved grease/oil stain removal especially at 70°F (21°C) is as follows.

<u>Ingredient</u>	<u>% (wt.)</u>
C ₁₄₋₁₅ EO(2.25) sulfate	15.33
C ₁₂₋₁₄ alkyl sulfate	5.67
30 C ₁₂₋₁₄ N-(3-methoxypropyl)glucamide	6.00
Citric acid	4.80
Fatty acids	3.00
Monoethanolamine	2.00
Ethoxylated tetraethylene pentamine	0.91
35 Protease	0.89
Boric acid	1.50

1,2-propane diol	10.00
Ethanol	7.00
Silicone suds suppressor	0.05
Water/miscellaneous	Balance

- 5 The foregoing composition is designed for use at 0.39 cup (92.4 mls) in a conventional U.S. top-loading automatic washing machine, or its equivalent.

EXAMPLE XII

- In addition to the use of the N-alkoxy surfactants herein in fully-formulated laundry detergents, it is useful to the commercial formulator to have such surfactants
 10 available as easily flowable and pumpable, ultra-high concentrated solutions which are stable on storage and stable to freeze-thaw cycles. The combination of up to about 75%, preferably up to about 55%, of the N-alkoxy surfactants with alcohols, typically 5%-20%, preferably 10%-12% and 1,2-propanediol, typically about 1%-10% and preferably with a soluble polycarboxylate such as citric acid, malic acid, maleic acid or
 15 the like, typically at levels of about 0.5%-3%, preferably about 2%, and water provides such compositions, as follows.

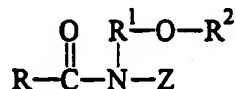
<u>Ingredient</u>	<u>% (wt.)</u>
C ₁₂₋₁₄ N-(3-methoxypropyl)glucamide	55.0
Ethanol	11.0
20 1,2-propanediol	6.0
Citric acid	1.0
Water	Balance

- The foregoing is a water-clear fluid with a viscosity (as measured above) of around 500. Useful compositions with viscosities in the range below about 1500 are
 25 prepared by varying the proportions of the ingredients listed.

- As noted hereinabove, the unique physical properties and cleaning performance of the N-alkoxy and N-aryloxy polyhydroxy fatty acid amides herein allow the formulation of effective detergent compositions containing little, or no, anionic surfactants. Thus, detergent compositions free of anionic surfactants, or at
 30 nonionic surfactant:anionic surfactant ratios in the range of from about 1:1, preferably about 2:1, to about 100:1 can be formulated.

In light of the foregoing, the present invention also encompasses a liquid laundry detergent, comprising:

- (a) an amide surfactant of the formula



wherein R is a C₇-C₂₁ hydrocarbyl moiety, R¹ is a C₂-C₈ hydrocarbyl moiety, R² is a C₁-C₈ hydrocarbyl or oxy-hydrocarbyl moiety, and Z is a polyhydroxy hydrocarbyl unit having a linear chain with at least two hydroxyls directly connected to the chain; and

- 5 (b) optional deterative adjuncts;
- (c) optionally, one or more anionic surfactants; and
- (d) a fluid carrier.

Preferred, compositions with little or no anionic surfactants preferably employ amide surfactants wherein R¹ is a C₂-C₄ alkylene moiety and R² is a C₂-C₄ alkyl moiety, especially wherein substituent -R¹-O-R² is a member selected from the group consisting of 2-methoxyethyl and 3-methoxypropyl and wherein R is C₁₁ and wherein Z is as defined above. Such compositions may additionally comprises a deterative adjunct ingredient which is a member selected from the group consisting of enzymes, builders, bleaches, soil release agents, optional auxiliary surfactants, dye transfer inhibiting agents, and mixtures thereof. Such compositions may comprise from about 15 1% to about 50% by weight of the amide surfactant, and are preferably provided in concentrated form comprising at least about 25% by weight of said amide surfactant. Optionally, the amide surfactant can be used in combination with conventional nonionics, such as the alcohol and alkylphenol ethoxylates, e.g., coconut alkyl EO(1-10). The invention also encompasses a method for cleaning substrates, comprising contacting said substrates with said composition in the presence of water, preferably at concentrations of amide surfactant of at least about 15 ppm.

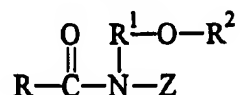
The following illustrates an "all-nonionic" laundry detergent composition herein, but is not intended to be limiting of such compositions.

25 EXAMPLE XIII

<u>Ingredient</u>	<u>% (wt.)</u>
C ₁₂₋₁₄ N-(3-methoxypropyl)glucamide	20.0
Ethanol	11.0
Citrate Builder	2.5
30 Protease	0.1
Cellulase	0.1
EDDS	1.5
Brightener	0.01
NaOH	to pH 9.8
35 Water, minors	Balance

What is claimed is:

1. A liquid laundry detergent, comprising:
 - (a) an amide surfactant of the formula



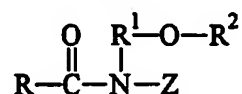
- 5 wherein R is a C₇-C₂₁ hydrocarbyl moiety, R¹ is a C₂-C₈ hydrocarbyl moiety, R² is a C₁-C₈ hydrocarbyl or oxy-hydrocarbyl moiety, and Z is a polyhydroxy hydrocarbyl unit having a linear chain with at least two hydroxyls directly connected to the chain; and
 - (b) one or more anionic surfactants; and
 - 10 (c) optional deterative adjuncts; and
 - (d) a fluid carrier.
2. A composition according to Claim 1 in concentrated form comprising at least 25% by weight of total surfactants.
3. A composition according to Claim 1 wherein R¹ is a C₂-C₄ alkylene moiety and R² is a C₂-C₄ alkyl moiety.
4. A composition according to Claim 3 wherein substituent -R¹-O-R² is a member selected from the group consisting of 2-methoxyethyl and 3-methoxypropyl.
5. A composition according to Claim 4 wherein R is C₁₁.
6. A composition according to Claim 1 wherein Z is a member selected from the group consisting of glucose, fructose, maltose, lactose, xylose and glycerol moieties, and mixtures thereof.
7. A composition according to Claim 1 which additionally comprises a deterative adjunct ingredient which is a member selected from the group consisting of enzymes, builders, bleaches, soil release agents, auxiliary surfactants, and mixtures thereof.
8. A method for cleaning substrates, comprising contacting said substrates with a composition according to Claim 1 in the presence of water.

9. A method for laundering fabrics according to Claim 8.

10. A flowable, pumpable concentrate, comprising up to 75% by weight of an N-alkoxy polyhydroxy fatty acid amide surfactant, an alcohol or diol solvent, and a soluble polycarboxylate material.

11. A liquid laundry detergent, comprising:

(a) an amide surfactant of the formula



5 wherein R is a C₇-C₂₁ hydrocarbyl moiety, R¹ is a C₂-C₈ hydrocarbyl moiety, R² is a C₁-C₈ hydrocarbyl or oxy-hydrocarbyl moiety, and Z is a polyhydroxy hydrocarbyl unit having a linear chain with at least two hydroxyls directly connected to the chain; and

(b) optional deterative adjuncts;

(c) optionally, one or more anionic surfactants; and

10 (d) a fluid carrier.

12. A composition according to Claim 11 wherein R¹ is a C₂-C₄ alkylene moiety and R² is a C₂-C₄ alkyl moiety.

13. A composition according to Claim 11 wherein substituent -R¹-O-R² is a member selected from the group consisting of 2-methoxyethyl and 3-methoxypropyl.

14. A composition according to Claim 13 wherein R is C₁₁.

15. A composition according to Claim 11 wherein Z is a member selected from the group consisting of glucose, fructose, maltose, lactose, galactose, mannose, xylose and glycerol moieties, and mixtures thereof.

16. A composition according to Claim 11 which additionally comprises a deterative adjunct ingredient which is a member selected from the group consisting of enzymes, builders, bleaches, soil release agents, auxiliary surfactants, dye transfer inhibiting agents, and mixtures thereof.

17. A composition according to Claim 11 in concentrated form comprising at least 25% by weight of said amide surfactant.

18. A method for cleaning substrates, comprising contacting said substrates with a composition according to Claim 13 in the presence of water.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/09550

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D1/65

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 9150, Derwent Publications Ltd., London, GB; AN 91-365819[50] 'Preparation of polyhydroxyamine fatty acid amide.' & JP,A,3 246 265 (KAO CORPORATION) 1 November 1991 cited in the application see abstract ---	1
A	WO,A,92 06162 (THE PROCTER & GAMBLE COMPANY) 16 April 1992 see page 7, line 13 - line 26 ---	1-18
A	EP,A,0 285 768 (HULS AG) 12 October 1988 see page 2, line 40 --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

3 November 1994

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 06172 (THE PROCTER & GAMBLE COMPANY) 16 April 1992 cited in the application see page 7, line 13 - line 19 see page 20, line 34 - page 21, line 31 ----	1-18
A	WO,A,92 06164 (THE PROCTER & GAMBLE COMPANY) 16 April 1992 see page 74, line 6 - page 75, line 3 -----	1-18

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/US 94/09550

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
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		CZ-A-	9300431	13-04-94
		EP-A-	0550557	14-07-93
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